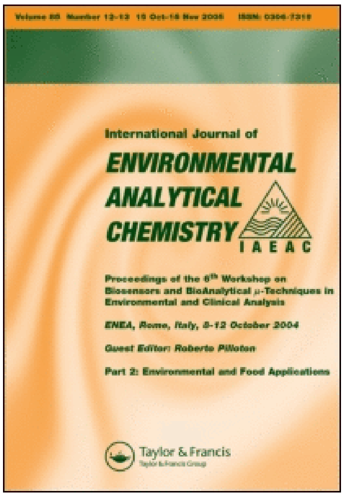

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On-Line Crossflow Filtration Coupled to Column Liquid Chromatography for the Determination of Triazines in Environmental Waters

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ON-LINE CROSSFLOW FILTRATION COUPLED TO COLUMN LIQUID CHROMATOGRAPHY FOR THE DETERMINATION OF TRIAZINES IN ENVIRONMENTAL WATERS

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Characterisation and selectivity of planar crossflow filtration membranes of 47 mm diameter for sampling and sample clean-up of environmental waters containing triazines and high levels of humic substances were investigated. The filtrate is collected in a sample loop, introduced to a column liquid chromatographic (CLC) separation system and quantified by UV-absorbance at 220 nm. Seven membranes, both cellulosic- and polymer types were investigated using samples with 10–80 mg/l of commercial humic acid. Triazine herbicides were chosen as model compounds together with other compounds of environmental concern such as p-nitrophenol and p-chlorophenol. The investigated membranes were found to interact in the filtration process. This led to large differences in terms of selectivity due to differences in pore size, hydrophobicity, porosity, and chemical structure of the membrane. The size and shape of the characteristic matrix front present in the obtained chromatograms were depending on the type of membrane used. In addition to these matrix effects, some of the membranes resulted in analyte recovery values of less than 100%. Repeatability and stability using nylon and PVDF membranes were evaluated as well as flux variances. An application with the optimised conditions in the CFF-LC-UV system for real surface water from a local creek was carried out with a resulting LOD of 1–5 μg/l (S/N = 3) using a 100 μl injection volume.

Keywords: On-line crossflow filtration; sampling; triazines; phenols; water

INTRODUCTION

Atrazine and related triazine herbicides are used throughout the world for the protection of crops from broadleaf weeds, on golf courses and for nonagricultural purposes such as soil sterilization and road maintenance. Both atrazine and

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simazine are biodegradated by microorganisms to their nonphytotoxic 2-hydroxy forms[1] and also to desisopropylatrazine and desethylatrazine[2]. Other possible breakdown products of pesticides are 4-nitrophenol and 4-chlorophenol[3]. The continuous monitoring of pesticides and transformation products in natural waters is of great importance in order to control the toxification of the environment. The legislation by law in terms of concentrations in the EU countries is 0.1 μg/l for an individual pesticide and 0.5 μg/l for total amount of pesticides in drinking water (no legislation for surface water exists). The development of methods for automated on-line sampling and sample clean-up techniques in natural waters is an important tool to enable this control and is therefore gaining increasing interest[4–7]. It also allows the on-site measurements to be carried out along water streams and to be used for early alarm systems.

Membrane filtration techniques such as cross flow, tangential flow, hollow fibre and dialysis are commonly used for rapid and efficient sampling[7–12]. After filtration a preconcentration step is commonly used to reach the low detection limits mentioned above. This step was investigated in an earlier study[13] where an integrated separation system using various solid phase extraction materials were characterised and used for the preconcentration of triazines in humic containing samples. The use of restricted access materials is one attempt to get cleaner samples in the enrichment procedure[13–17]. However, to avoid clogging and column saturation in continuous monitoring, a filtration step was found to be of mandatory importance to eliminate solids, colloids and other particular matters. The crucial sampling step were for these reasons thoroughly investigated. To make trace level determinations of organic pollutants in complex matrices appropriate validity of the sampling and sample handling must be ensured[18–20].

The filtration step can be carried out by different means, at-site by the river or in the laboratory after sample transport in either bottles or on SPE materials. The goal is to get as clean filtrates as possible, giving sample chromatograms with less influence from matrix interferences. This would result in determinations with better precision and accuracy as well as simplifying determination of polar analytes. Normally filtration is used as a first step in many analytical methods without considering irreproducibility due to losses from membrane interactions upon filtration. This paper presents the importance in choosing an appropriate membrane for continous use in environmental measurements. Outlines for membrane conditioning is also presented.

MATERIALS AND METHODS

Chemicals

Humic Acid, $M_w \sim 600–1000$ from Fluka (Buchs, Switzerland); acetonitrile and dihydrogen sodium phosphate, purchased from Merck (Darmstadt, Germany); 2-hydroxy-simazine, certified C–169550 Lot 40322; desisopropyl-atrazine, E–103320 Lot 30128; desethyl-atrazine, E–103310 Lot 30505; 2-hydroxyatrazine, E–103330 CH 21123; atrazine, IPO 005 and simazine, IPO 692 were all purchased from Dr. Ehrenstorfer (Augsburg, Germany). 4-nitrophenol Lot 867198 and 4-chlorophenol were purchased from Merck (Darmstadt, Germany). All other chemicals were of HPLC grade and the solutions were made with millipore water (Bedford, MA, USA). Stock solutions were prepared in methanol (stored in dark at + 4°C) and from these standards, sample solutions of the pesticides were made daily. Buffer solutions were filtered and degassed under vacuum 15 minutes before use. The humic acid matrix solutions were prepared by dissolving the humic acid in millipore water.

Instrumental

A schematic overview of the complete system is shown in Figure 1. A peristaltic pump Miniplus 2 or a HPLC piston pump Model 306 (Gilson Instruments, Villiers-le-Bel, France), were used to pump the sample solution over the membrane which is placed in a Filter Acquisition Module (FAM) (Waters, Bedford, MA, USA). The filtration unit was coupled to and controlled from a solvent delivery module Model 590 (Bedford, MA, USA). The sample filtrate is collected in a sample loop of 100 µl that is mounted into a six-port Rheodyne switching valve (Rheodyne, Cotati, CA, USA). At injection the valve is switched and the sample is transported to the liquid chromatography system using an analytical column, LiChrospher 100 RP-18, 5 µm, 125 × 4 mm I.D. from Merck (Darmstadt, Germany). A guard column of the same packing material was used to prolong the lifetime of the analytical column. A UV-Vis detector Model 119, (Gilson Instruments, Villiers-le-Bel, France) was used for the detection. The different membranes (all with 47 mm diameter) tested were HAWP04700, Cellulose Esters (0.45 µm pore size) and GVWP04700, PolyVinylideneDiFluoride (PVDF) (0.22 µm) were purchased from Millipore (Bedford, MA, USA) and further A045047A, Cellulose Nitrate (0.45 µm); C045A047A, Cellulose Acetate (0.45 µm); J050A047A, Teflon, 0.5 µm; P13013 PolyCarbonate (PC) screen membrane (0.2 µm) and finally 83052, 4-6-Nylon (0.45 µm) were all gifts from

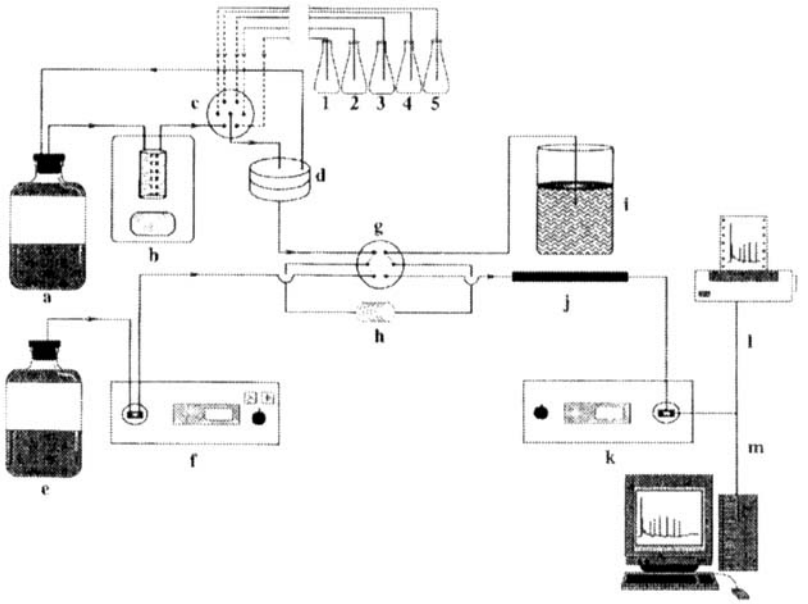


FIGURE 1 Shematic overview of the entire setup. The abbreviations stands for a) sample b) peristaltic pump c) solvent delivery valve for various regeneration solutions (1–5) and sample solution d) Filter Acqusition Module (FAM) e) mobile phase f) HPLC-pump g) switching valve h) sample loop i) waste j) analytical column k) UV-detector l) recorder and m) computer

AKA-ARL Filter AB (Helsingborg, Sweden). A software program Baseline 810 (Millipore, Bedford, MA, USA) was used for data handling.

Experimental Procedure

The sampling was done by pumping the sample solution over the membrane and creating a pressure difference. The sample is filtered through the membrane for 10–15 minutes to avoid solute transport variations to and from the surface before injection. When the loop is filled with a representative sample, the six-port valve is switched and the sample is transported with the mobile phase to the analytical column in the LC-system. The separation was achieved using an isocratic mobile phase (23:77 acetonitrile/50 mML/phosphate buffer pH 6.5) at a flow rate of 0.9 ml/min and a reversed phase LiChrospher C_{18} analytical column. The response from the connected UV-detector was recorded on a stripchart recorder and collected on the computer simultaneously. The membrane was taken out and replaced during the separation of the analytes.

RESULTS AND DISCUSSION

The separation mechanism of microfiltration is based on transport of small molecules across a membrane. The membrane pore size varies between 0.1–5 μm whereas membranes used in ultrafiltration have 1–10 nm pore sizes, roughly corresponding to a nominal molecular weight cut-off (NMWCO) of 1–500 kD. The transport of solutes through the membrane barrier occurs because of a pressure difference ΔP, that is built up across the membrane when pumping a solution in the cross-flow mode. This pressure depends on the solution feed rate, the position of the built-in restrictor, and the dimensions of the outlet tubings. Molecules and particles larger than the membrane pore size do not pass through the membrane. They are excluded and swept away by the liquid stream to the waste. The conventional filtration units, with the sample flow perpendicular to the membrane also referred to as dead-end flow or impact flow, are not well suited for large volume samples with high humic acid concentrations. Since the solid particles and colloids cause a material build-up on the membrane surface and a deposition of dissolved and/or suspended solids inside the membrane, resulting in a decrease of the flux transport rate and finally to total blocking of the membrane. For small volumes though, the simplicity of this straight forward technique can be an advantage as long as no analyte losses occur. For on-line filtration of larger volumes, crossflow filtration is preferable and is frequently applied. Except the flatsheet membranes investigated in this study, common designs for crossflow filtration include tubular (r > 0.635 cm), capillary (0.1–0.635 cm) and hollow fibers (0.025–0.1 cm). The flux through a microfiltration membrane can be expressed as:

$$J = \frac{\Delta P}{\eta \cdot R_{tot}} \tag{1}$$

where J = flux, ΔP = pressure, R_{tot} = total resistance of the filtration system and η = viscosity. Flux measurements were carried out with the various membranes and the result is shown as filtrate rate (ml/min) in Table I. The flux differences at each feed rate were found to be rather small when using millipore water samples. Generally, the pore size was expected to be the main factor to these variations. However, PVDF membranes resulted in the highest flux 2.6 ml/min at 12 ml/min feed rate although having the smaller pore size of 0.22 μm, while polypropylene membranes with a pore size of 0.6 μm gave the lowest flux 1.5 ml/min. These variations could be due to structural differences e.g. polypropylene is characterised as hydrophobic while the PVDF is hydrophilic.

In order to increase the flux through the membrane, and thereby reduce sampling time, an experiment with a cellulose based and a polymer based membrane

TABLE I Flux variations for various membrane materials using different pump feed rates

Filter type *Size (μm)*	*Feed rate (ml/min)*	*flux (ml/min)*
Cellulose ester	12	2.0
(0.45)	9	1.5
	6	1.0
Polypropylene	12	1.5
(0.6)	9	1.05
	6	0.7
Nylon	12	1.9
(0.45)	9	1.4
	6	0.9
Cellulose nitrate	12	1.6
(0.45)	9	1.15
	6	0.8
Teflon (PTFE)	12	1.8
(0.5)	9	1.3
	6	0.85
Cellulose acetate	12	1.75
(0.45)	9	1.30
	6	0.85
Polyester scr. membrane	12	1.75
(0.4)	9	1.25
	6	0.8
Polycarbonate scr. membrane	12	2.4
(0.2)	9	1.5
	6	0.8
Polyvinylidene difluoride	12	2.6
(0.22)	9	1.8
	6	1.1

was carried out by using higher feed rates i.e. by increasing ΔP. It was found that the cellulose based membrane broke when feed rates higher than 40 ml/min was applied, while the PVDF membrane showed such a mechanical strength that up to 75 ml/min of feed rate (giving a filtrate rate of 11 ml/min) was possible without breaking the membrane. The FAM-unit has a built in restrictor that controls the pressure difference over the membrane but since it was totally open, no further increase in flux rate was possible. Other ways to increase the flux is to decrease the I.D. of the outlet capillary or by changing the size of the CFF module e.g. from 47 to 90 mm in diameter, giving a fourfold increase in membrane area and reducing the sampling time considerably.

It is well known that the filtrate flow or the flux, decreases with time during constant sampling. This occurs since the R_{tot} in equation (1) increases during filtration. We investigated this parameter by taking the two best operating membranes Nylon and PVDF for long-time experiments. A humic acid solution of 10 mg/l was recirculated across the membrane for 24–48 hours with constant filtration (restrictor open). Figure 2 shows how the flux or filtrate flow through the Nylon membrane reduces very fast with time, probably due to a material build up on the membrane surface, which is a major disadvantage for the sampling step. This build-up on the membrane surface could be seen upon de-assembling the membrane unit and weighing the membrane after use. Using 40 mg/l humic acid solution and pumping for one hour resulted in 25 mg solid matter precipitation on the nylon membrane. As much as 98% of this precipitation could be removed by regenerating the surface. This was achieved by closing the restrictor that controls the pressure difference over the membrane and pump millipore water along the membrane between the simulated sampling occasions. The impact of this procedure on the flux decrease is also shown in Figure 2. It is obvious that the flux can be held constant for a long period of time, giving oppurtunities to combine the filtration process with on-line trace enrichment steps such as solid phase extraction. Additional experiments with methanol as an extra regenerating solvent was made, resulting in a more powerful regeneration which also remove water insoluble matter.

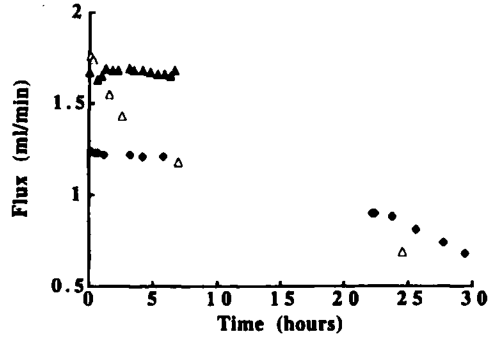


FIGURE 2 Flux decrease when using constant crossflow filtration of a 10 mg/l humic acid with (Δ) nylon and (♦) PVDF membranes respectively. Influence of regeneration with millipore water between the sample measurements using nylon membranes without (Δ) and with regeneration (▲)

In the ideal case R_{tot} in equation (1) is equal to R_m (membrane), which means that the resistance against mass transfer is only caused by the membrane with contributing factors like membrane thickness, nominal pore size, hydrophobicity, and various morphological features like tortuosity, porosity and pore-size distribution. The membranes investigated are of the porous (cellulose-based, nylon, teflon and PVDF membranes) and non-porous (screen membranes) type. Among these, the non-porous two-dimensional screen membranes have the most simple structure.

Since the membrane has the ability to transport one component more readily than others because of differences in chemical and/or physical properties between the permeating solutes and the membrane, or in some cases completely retain the solutes, there will be an accumulation of retained molecules near the membrane surface. This results in a highly concentrated layer near the membrane which exerts a resistance towards mass transfer i.e. the concentration polarization (cp) resistance R_{cp}. This always occurs and is inherent to membrane separation processes.

The concentration polarization gives a steady-state condition when the convective transport of solute to the membrane is equal to the sum of the filtrate flow plus the diffusive back transport of the solute. When performing the cross-flow filtration experiments, the filtrate is therefore not collected for CLC-analysis immediately but after approximately 10 min. This is important in order to control the influence of R_{cp} as much as possible. Several possibilities to reduce R_{cp} are available e.g. hydrodynamic methods. Some examples are pulsating flow, reversed flow, cleaning solutions and turbulent flow which can be formed by using inserts, vortices or rough surfaces. Other processes that can occur and affect the filtration process are gel layer formation, pore blocking and adsorption. These are mainly reduced by just using the cross-flow filtration technique.

Recovery Studies

Ideally, no recovery losses should occur during the sampling procedure. Therefore, there should not be any interactions between the analytes and the membrane, recovery values close to 100% should be obtained in order to get a satisfying sampling procedure. There are two main reasons for this assumption, first the pore size is much larger than the size of the analyte and second the amount of membrane material in the porous membrane which might interact with the analytes is limited. The possible sites for adsorption will be occupied rather quickly, causing an increase of the analyte concentration with time.

A 40 μg/l mixture of the pesticides were run with the various membranes at different feed rates using millipore water. We calculated the recovery which is defined as the response ratio between filtrated sample and a direct injection. There was no significant difference in the recovery values found at 6, 9 and 12 ml/min feed rate and the recoveries were as expected approximately 100% ($n = 3$, RSD < 10%) for all the membranes.

Complex Humic Acid Containing Samples

As stated before, the membranes are not allowed to interact with the analytes and the ideal case would be a total removal of the matrix. The possibility to remove matrix interferences by CFF using different membrane materials was investigated by analysing three concentration levels of analytes and humic acid respectively. Despite the well-known fact that commercial humic acids are a poor substitute for the variety of real-world humic substances encountered it was selected in this study. The lower molecular weight fraction (600–1000) of humic acid (HA) particles used in this study, are far to small to be excluded from the membrane pores. Nevertheless, solids and colloids which are aggregates in the reference humic acid are prevented to pass the membrane barrier. Three repetitive injections at analyte concentrations of 40, 100 and 200 µg/l were made and the RSD-values varied between 0–10% with most variation when using water with the highest concentrations of humic acids. The results presented in Table II gives a mean recovery of 9 injections (RSD < 10%), since there was little variation within one matrix. The concentrations of the chosen humic acid were 10, 40 and 80 mg/l, which is more than relevant in comparison with the expected values in natural waters (0.1–50 mg/l)[21]. The complexity of the brown-coloured samples is high i.e. the 10 mg/l solution corresponds to an absorbance value of 0.3 a.u. at 220 nm. Only one injection was made at 80 mg/l HA, since the analytical column was detoriated using this sample matrix. Some values are above 100% arising from difficulties in the integration of non-filtered samples. Since the recovery values in Table II do not include interactions between analyte and matrix, comparison between directly injected non-filtered samples of millipore- and HA matrices gave an estimation of the degree of binding to the humic acid. It was approximately 0–10%, with a tendency of higher values at low concentrations of analytes.

TABLE II Recovery values for pesticides in humic acid matrices of 10, 40 and 80 mg/l. Three concentrations of analyte was studied and the mean value of these measurements are shown. Results that are of special interest are printed in bold

Filter type	*[HA]*	*HYS*	*DIA*	*HYA*	*DEA*	*NP*	*SIM*	*CP*	*ATR*
Cellulose ester	10	96	93	92	97	**79**	99	**85**	99
	40	95	97	101	107	95	104	95	103
	80*	–	–	–	101	101	104	93	107
Durapore	10	94	97	96	100	101	103	106	103
	40	104	111	106	103	113	107	113	106
	80*	–	–	93	106	114	110	106	106
Cellulose Acetate	10	93	94	95	98	**62**	96	**61**	85
	40	97	97	104	103	**74**	99	**66**	87
	80*	–	–	–	106	**93**	107	**79**	98
Teflon	10	**87**	101	**80**	103	106	103	111	102
	40	**89**	105	**57**	104	108	100	108	96
	80*	–	–	–	98	100	98	88	91
Cellulose nitrate	10	90	98	99	100	**79**	99	**88**	100
	40	102	101	98	98	**82**	98	**86**	99
	80*	–	–	–	99	**85**	104	**87**	101
PolyCarbonate Screen	10	98	99	101	102	104	104	103	105
	40	100	106	102	105	108	106	105	105
	80*	–	–	80	100	100	106	96	105
Nylon	10	105	103	99	103	103	103	106	105
	40	103	109	103	105	109	104	105	102
	80*	–	95	82	101	100	104	95	102

*Only one injection.

Calibration curves for each analyte were made and by overlapping the calibrationbration curves obtained using different membranes, it is clearly seen that some of the membranes had lower recoveries for especially two compounds (p-nitrophenol and p-chlorophenol). These membranes were cellulose acetate (CA), mixed cellulose esters (CE) and cellulose nitrate (CN), see Figure 3 a-b. For comparison, the ideal behaviour of DEA is shown in Figure 3 c, where the same calibration graph is obtained on all membranes tested. The CE membrane consists of a mixture of CA and CN, which can explain its similar behaviour to the CA membrane. It has been shown before by Kiso et al[22] that CA can bind organic compounds, but this is not a satisfying explanation to the results obtained, since without the humics there is no such binding occurring. It is possible though, that the modified membrane surface changes the complex equilibrum of bound and unbound analytes in the filtration system and thereby also the adsorption properties. As shown in Table II, the teflon (PTFE) membrane resulted in low recoveries for the hydroxy-metabolites and there is also a tendency of low recoveries for atrazine using the cellulose acetate membrane. The recovery of p-nitrophenol and p-chlorophenol with the cellulose acetate membrane were approximately 70%, which indicates that these membranes are not so applicable for filtration when determining these phenols.

The interesting outcome of this experiment was not only the lower recoveries for some of the compounds when using a certain membrane, but also that the membranes gave different filtrate composition. This was observed as various chromatographic frontal peaks where some membranes reduced the HA matrix peak more than others. In Figure 4, performance of the best and the worst membrane are shown together with a direct injection of a millipore solution. Obviously, by using nylon as membrane material it is possible to reduce the matrix peak and clearly determine more compounds with higher precision and accuracy. This reduction of humic interference will be of mandatory importance when coupling to a pre-concentration step is made. Cleaner samples would result in cleaner extracts and much smaller interferences in the obtained chromatograms enhancing both stability, sensitivity, selectivity and precision. One explanation to why this reduction is occurring could be that the protein binding capacity for nylon membranes are much greater than the other membranes. This causes the humics to bind to the membrane, thereby lowering matrix effects of the filtrate. During filtration over a long time, this effect should gradually decrease. However, when making 10 repetitive injections (RSD $< 4\%$), no such decrease was observed.

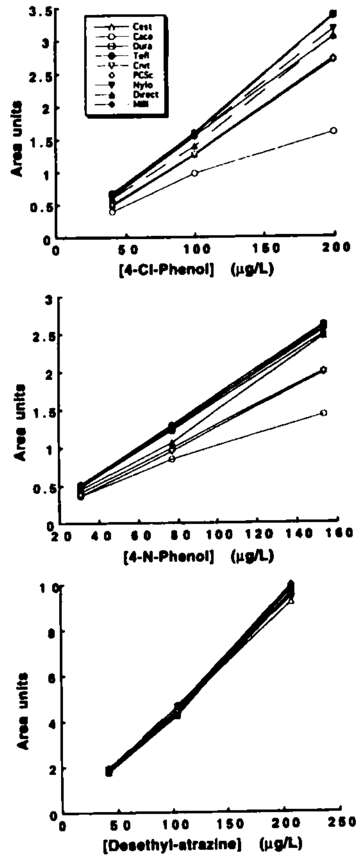


FIGURE 3 Calibration curves for a) 4-chlorophenol b) 4-nitrophenol and c) desethylatrazine using a 10 mg/l humic acid matrix with various membranes

Scanning Electron Microscopy

To obtain more information about the membrane fouling processes, scanning electron microscopy (SEM) was used for a thorough investigation of nylon and CA membranes. A sample solution of 40 mg/l humic acid and 40 µg/l pesticides was filtered for 0 (flush of millipore water), 0.5, 3, and 16 hours, respectively. Figure 5 a-e illustrates the fouling process at different stages of filtration. The complex three-dimensional structures and the surface of the membranes can be observed from these electron micrographs. It seems like the pore sizes are not equal as the nylon pores are significantly smaller than the pores of CA. Further comparisons show that the fouling process becomes a serious problem at an ear-

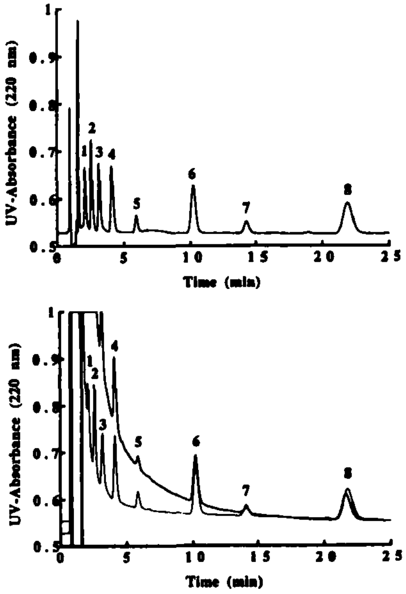


FIGURE 4 Separation of analytes at 40 μg/l using: (a) millipore solution of a pesticide mixture at 40 μg/l, (b) the same sample mixture but with 40 mg/l of humic acid after cross flow filtration using cellulose acetate (upper chromatogram) and nylon membranes. The chromatographic peaks representing 1) hydroxysimazine 2) desisopropylatrazine 3) hydroxyatrazine 4) desethylatrazine 5) 4-nitrophenol 6) simazine 7) 4-chlorophenol 8) atrazine

lier stage (0.5 h) using CA, whereas nylon membranes starts to foul some- where between 3 and 16 hours of use. After 16 hours it is easily seen that both membranes are fouled, this is seen as spots of clogging are visible at various places and to a varying extent on the membrane surface. It should be stated that the membranes in this study was continuously filtered and only flushed with millipore water afterwards to remove the fraction of the fouling layer that would be removed after regeneration.

Repeatability and Stability

It is very important to have a constant filtrate composition during the sampling, giving the correct composition of the sample. To investigate the repeatability of the filtrate composition in terms of the selected analytes as well as matrix components, 10 repetitive injections from a 10 μg/l humic acid solution were made with the nylon and the PVDF membranes. The RSD-values of the chromatographic peaks, were less than 4% for both membranes investigated. The stability of the analytes in millipore water (stored at 4°C) was investigated by injecting a

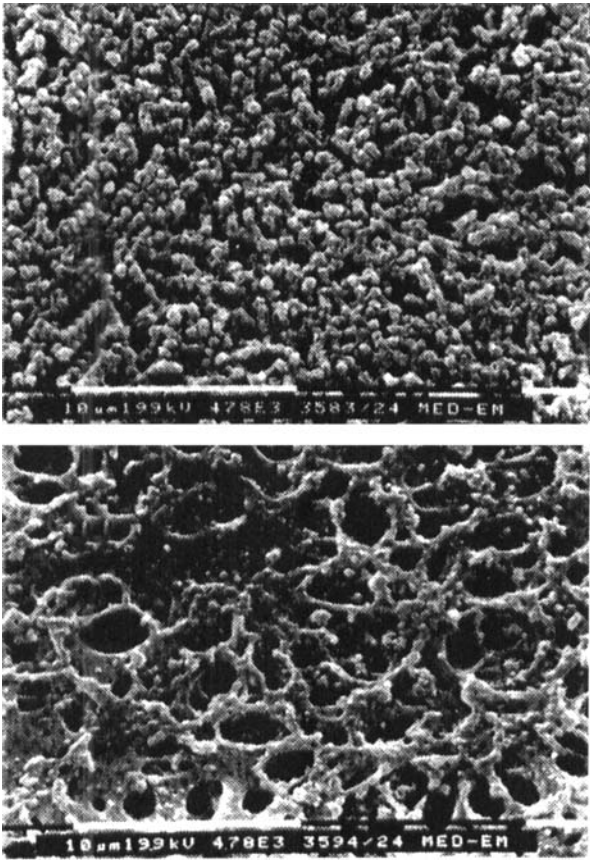
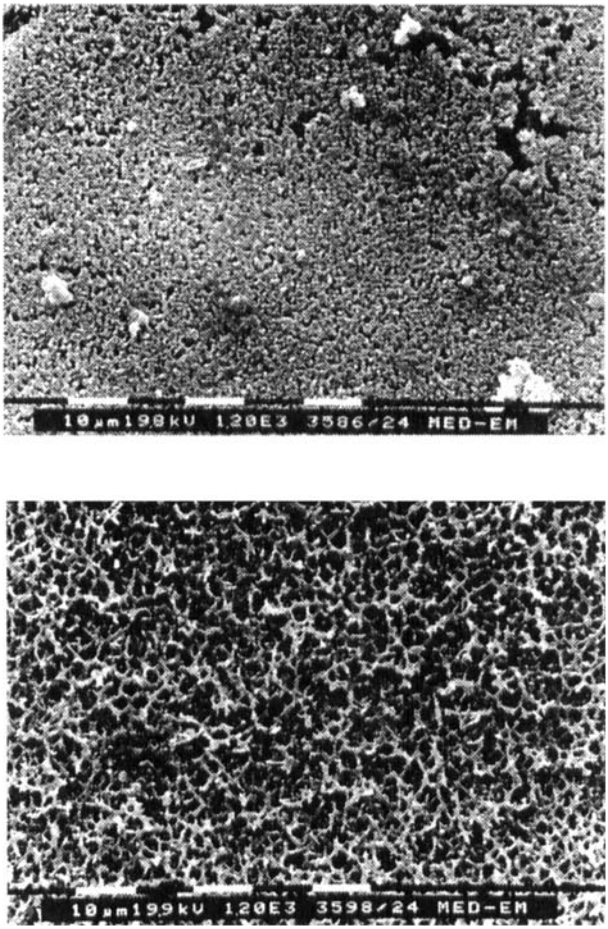


FIGURE 5a-b Scanning electron micrographs of microfiltration membranes after cross flow filtration of 40 mg/l humic acid containing pesticide samples. a) Nylon membrane after 0.5 hours of use 4780x b) cellulose acetate membrane after 0.5 hours of use 4780x c-d) clogging of nylon and cellulose acetate membranes after 16 hours of use 1200x and finally e) magnification of a clogging spot on a cellulose membrane 4780x

40 µg/l pesticide mixture every day before starting the other experiments. In this way both the chromatographic system and the stability of the compounds were controlled continuously. There was no significant decrease in response or chromatographic behaviour during a period of 20 days, which speaks for a good stability of the analytes (in water) investigated as well as the chromatographic system.

The optimised system was applied using the nylon membrane for crossflow filtration of spiked creek water (local creek outside Lund) on-line coupled to liquid chromatography and ultraviolet detection. This water was slightly coloured and probably did not contain much HA. However, the system worked adequately and the detection limits were between 1–5 µg/l (CV = 4%, n = 10) for the various pesticides.



FIGIRE 5c-d (continued)

CONCLUSIONS

We have been able to show that a proper choice of membrane, membrane/sample interactions give rise to fouling, concentration polarisation and other effects. Unpredictable and varying recovery values for s-triazines and phenols could then be obtained. Matrix components such as humic substances and other interferents appear as a chromatographic front in HPLC-UV analysis. This causes some chromatographic resolution problems, especially when determining polar analytes and here the membrane choise is of significant importance. In this study, this was clearly demonstrated by the comparison of the nylon 46 and the cellulose acetate membrane. Since the sample matrix variances are large (season of the year, ground and soil type etc.) there can be no general rules in determining the effect upon the filtration process. Each type needs to be pre-processed for selectivity evaluations. The pre-requirement should be that recoveries around 90–100% should be achieved for sample analytes in longer time perspectives. At lower values additional mechanisms might be involved in the membrane/sample filtration process, which might be difficult to keep control of. A limited number of standard humic containing waters and creek water were studied. Future studies to apply the optimised on-line sampling procedure to a number of environmental waters with varying complexity will be outlined. The step from the laboratory to filtration in the field would demand extended sampling time and unattended operation. Extended sampling time, maintaining high and stable recovery data would be possible by using the regeneration step as described. The filtration itself will be totally automated with the exception of exchanging membranes, which would be necessary to do on a daily basis. For prolonged stability of the chromatographic system, we used a guard column to protect the analytical column. With the current setup, the guard column was exchanged every two weeks and the lifetime of the analytical column in these complex matrices was estimated to be around six months.

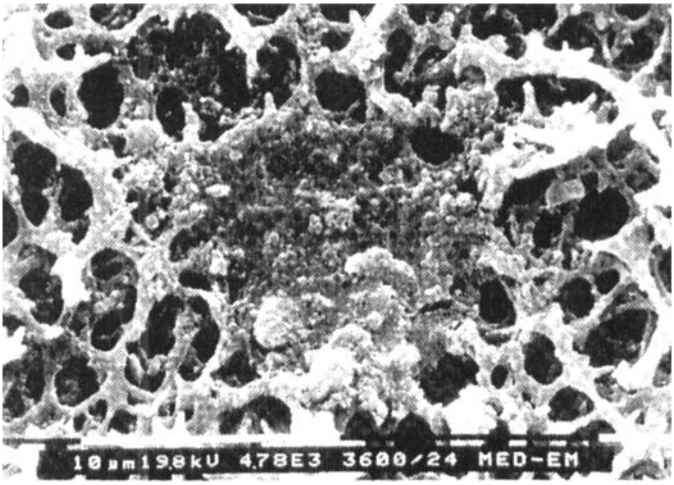


FIGURE 5c

Acknowledgements

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